Influence of the Amount of Silane Coupling Agent on the Dielectric Properties of AlN/Polypropylene Nanocomposites

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***Abstract*- In this work, four loading amounts of trimethoxy (octyl) silane (C8-M) were used in preparing C8-M treated AlN/polypropylene nanocomposites. Although the thermal gravimetric analysis shows a significant difference in the amount of C8-M grafted on the AlN surface, and a saturation point can be reached as the amount of C8-M added increases, the AC breakdown strengths of composites present virtually identical results. Similar behaviours can be observed in the real and imaginary permittivity from 0.01 Hz to 100 kHz, although the upturns of the imaginary permittivity at low frequency are observed increasing with the amount of C8-M used. Seemingly contradictory to a previously reported work on epoxy with nanosilica, AlN/polypropylene is largely unaffected by the amount of the silane coupling agent applied during the surface treatment.**

***Keywords*- nanocomposites; polypropylene; silane coupling agent; AC breakdown strength; permittivity**

I. INTRODUCTION

Silane coupling agents (SCA) are commonly applied to improve the dispersion of nanoparticles and minimise the incompatibility between organic and inorganic materials [1-4]. In polymer nanodielectrics, the addition of SCA can displace the hydroxyl groups on the particle surface and mitigate the water absorption issue [5, 6]. Relatively little research has been done on the influence of the amount of SCA used during the sample preparation. Although an estimation method based on the number of bonding sites for SCA on the particle surface to find the optimum quantity was proposed by some research works, the SCA loading amount is often derived empirically [1, 3]. It was reported that an excess amount of SCA could degrade the AC breakdown strength of the nano-silica/epoxy system [1]. On the other hand, an insufficient amount of SCA can lead to an inadequate particle dispersion and an insufficient coating on the nanoparticle. Present work focuses on investigating the effect of the amount of SCA on the dielectric properties of nanocomposites. In this paper, a commonly used SCA was selected to study the effect of its loading amount on the AC breakdown strength and dielectric response of AlN/polypropylene nanocomposites.

II. EXPERIMENTAL

A. Materials

Trimethoxy (octyl) silane (C8-M) with a relative density ρ=0.907 g/ml (at 25 °C) and AlN (~50 nm) were obtained from Aladdin industrial Inc. Isotactic polypropylene (average M_w ~340,000, average M_n ~97,000) was purchased from Sigma Aldrich, with a transition temperature T_m=160-165 °C.

B. Surface functionalisation of AlN

The amount of SCA used in the preparation procedure is required before the surface functionalisation of AlN is operated. An estimation method in [3] use thermogravimetric analysis (TGA) to estimate the amount of the bonding sites, -OH groups, and giving the amount of SCA needed for bonding is applied here. The amount of C8-M required can be approximately estimated by the density of the surface -OH groups of AlN when assuming these hydroxyl groups can be displaced entirely by C8-M. The hydroxyl groups on the AlN surface will usually start to lose around 446.85 °C and cannot be fully removed up to 700 °C but with a very low density [3, 7]. Before AlN is tested by TGA, it was added to dry toluene due to the safety procedure. Therefore, the AlN and toluene mixture was isothermally dried at 110.6 °C for 1 hour before heated from 50 to 900 °C at an increasing rate of 10 °C/min. From the TGA result shown in Fig. 1a, the weight decreased by 0.7 % in a temperature range from 446.85 to 700 °C. That means the density of hydroxyl groups is about 7 mg per gram of AlN. How many -OH groups in 1 g of AlN can be computed by Equation 3, where N_A is the Avogadro number, m_{-OH} and M_{-OH} are the mass and the molecular weight of the -OH group respectively.

$$N_{-OH} = N_A \cdot v_{-OH} \tag{1}$$

$$v_{-OH} = \frac{m_{-OH}}{M_{-OH}} \tag{2}$$

$$N_{-OH} = N_A \cdot \frac{m_{-OH}}{M_{-OH}} \tag{3}$$

$$N_{-OH} = 6.02 \cdot 10^{23} \cdot \frac{7 \cdot 10^{-3}}{17} = 2.5 \cdot 10^{20} \tag{4}$$

$$N_{C8-M} = \frac{N_{-OH}}{3} = \frac{2.5 \cdot 10^{20}}{3} = 8.3 \cdot 10^{19} \tag{5}$$

Ideally, one SCA can form bonds with three hydroxyl groups, then the required number of SCA molecules is $N_{C8\text{-}M} = 8.3 \cdot 10^{19}$ per gram of AlN. The volume of C8-M to react with 1 g of AlN, $V_{C8\text{-}M}$, can be calculated by Equation 8, where $M_{C8\text{-}M}$ and $\rho_{C8\text{-}M}$ are the molecular weight and the density of C8-M, respectively. However, the condensation of SCA and the loss of SCA on the equipment make the actual amount needed to be more than the calculated value. So, the obtained value is often multiplied by a multiplication factor n. As shown in Equation 10, the volume of C8-M used for 1 g of AlN, $n \cdot 0.036$ ml, can be obtained.

$$m_{C8-M} = M_{C8-M} \cdot \frac{N_{C8-M}}{N_A} \tag{6}$$

$$V_{C8-M} = \frac{m_{C8-M}}{\rho_{C8-M}} \tag{7}$$

$$V_{C8-M} = \frac{M_{C8-M}}{\rho_{C8-M}} \cdot \frac{N_{C8-M}}{N_A} \tag{8}$$

$$V_{C8-M,multiplied} = n \cdot V_{C8-M} = n \cdot \frac{M_{C8-M}}{\rho_{C8-M}} \cdot \frac{N_{C8-M}}{N_A} \tag{9}$$

$$V_{C8-M,multiplied} = n \cdot \frac{234.41}{0.907} \cdot \frac{8.3 \cdot 10^{19}}{6.02 \cdot 10^{23}} = n \cdot 0.036\, ml \tag{10}$$

Dry toluene is a rational choice for the anhydrous route as its non-polar nature and low level of water content can limit the reversibility of the bond formation and the formation of a thick polysiloxane layer on the nanoparticle surface by the condensation of SCA [4, 8]. 3 $Å$ molecular sieves were added to toluene in a ratio of 0.2g/ml with a drying time of 2 days. The surface functionalisation procedure was detailed in [9], but the amount of SCA used in this work is different. Four multiplication factors were selected, and the amounts of C8-M used for 2 g of AlN are listed in Table 1.

C. *Blending*

AlN/polypropylene nanocomposites were made by a solution blending method with 10 wt. % of AlN. After the surface treatment, the C8-M treated AlN was dissolved in toluene, a 5 min of sonication by a sonication bath was applied to break the agglomerations. After that, 0.5 g of AlN in 10 ml of toluene was added to 50 ml of boiling xylene with 4.5 g of dissolved polypropylene. The resulting mixture was stirred until it becomes solid. It was then cut and dried in a fume cupboard for 1 day. Before the samples were dried in a vacuum oven at 80 °C for 3 days, they were pressed into sheets. They were then pressed into different samples for dielectric tests at 180 °C after drying. Four dielectric systems were prepared at the end. They were denoted by "C8-*n*" for brevity, e.g. the polypropylene filled with 10 wt. % of C8-M treated AlN with the multiplication factor *n*=7 was used during the surface treatment is denoted as "C8-7".

D. *Characterisation*

A Perkin Elmer Pyris 1 TGA was applied to test the amount of SCA on the surface of nanoparticles from 50 to 900 °C at a rate of 10 °C/min in nitrogen. Film samples (120±10 μm) were clamped between two aligned spherical electrodes, with an AC voltage ramped up at 500 V/s until a breakdown occurs. Dielectric spectroscopy tests in a frequency range of 0.01 Hz to 100 kHz were used to analyse the dielectric response of each system and a Solartron 1296 system linked with a Schlumberger SI 1260 analyser was applied to measure gold-coated samples with a thickness of 230±10 μm.

TABLE 1
C8-M USED FOR SURFACE FUNCTIONALISATION

Multiplication factor *n*	C8-M for 2 g of AlN (ml)
1	0.07
7	0.50
15	1.08
30	2.16

III. RESULTS AND DISCUSSION

A. *TGA results*

The TGA results of the AlN treated with different amounts of C8-M are shown in Fig. 1 and 2. The AlN treated without SCA have 97.0 % of weight remain after heated to 900 °C in Fig. 1a and a broad peak at 196.8 °C can be observed on the derivative curve, which often assigned to the dehydration of the surface hydrolysed layer [10]. In Fig. 1b, a broad peak from 200 to 600 °C can be observed on the derivative curve and peaked at 428.4 °C, which is assigned to the grafted C8-M on the AlN surface [9].

In Fig. 2a, for the AlN treated with 1 and 7 parts of C8-M, the weight remain after heated to 900 °C is decreasing from 95.4 to 93.2 % as the SCA loading amount is increasing. However, no obvious decrease can be observed when increasing the multiplication factor *n* from 7 to 30. These results indicate that there might be a saturated point between *n*=1 to 7. Consistent results are shown in Fig. 2b, where a significant increase in the magnitude of the peak shows on derivative curves can be observed when increase *n* form 1 to 7, and the results are identical when *n*=7, 15 and 30.

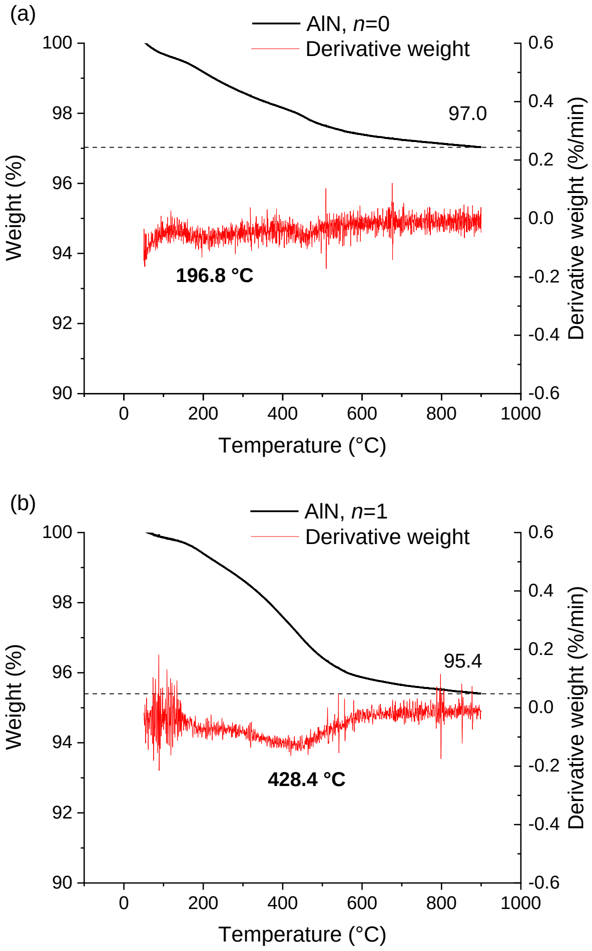

Fig. 1. TGA results of AlN treated with different amounts of C8-M when (a) *n*=0 and (b) *n*=1

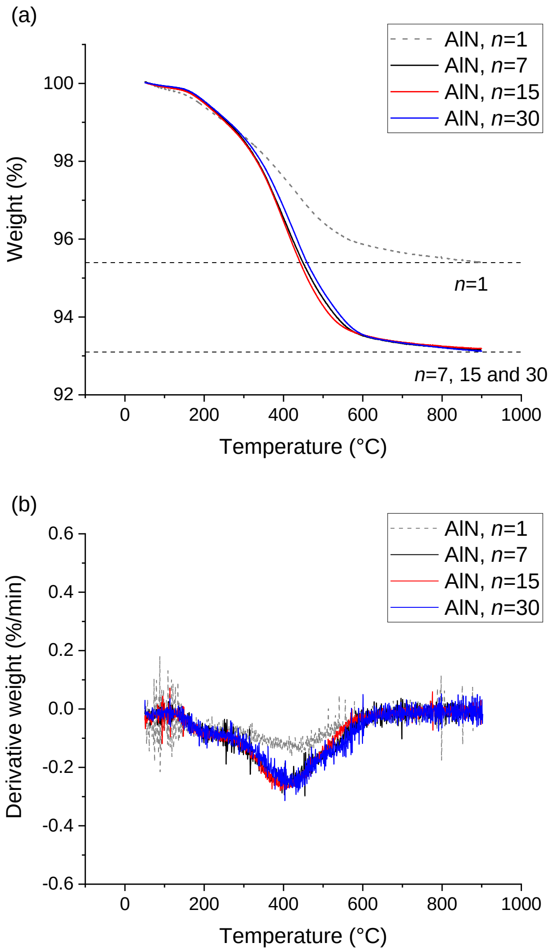

Fig. 2. TGA results of AlN treated with different amounts of C8-M, (a) weight remain and (b) derivative curves

Assuming the specific surface area of the nano AlN is 20 m^2/g (according to the datasheet and taking into account the agglomeration effect) and the -OH groups are evenly distributed on the surface, the thickness of the bonded SCA layer can be estimated with the help of the residue weights from TGA results. From the estimated thickness of the C8-M layer in nanocomposites listed in Table 2, the thickness of the C8-M layer is less than 1 nm (e.g. a single layer of C8-M) when n=1. This result indicates that the nanoparticle surface might not be fully covered by C8-M in this case. Although there seems to have a saturation point when increasing the amount of the SCA applied, it is hasty to conclude that a single layer of C8-M is formed surround AlN when a sufficient amount of C8-M is used, i.e. n=7, 15 or 30. As the tri-bonding site structure of C8-M, it is possible to form a network around nanoparticles by the condensation process, even the anhydrous method was applied [1]. It is worth to note that the volume ratio of the surface layer can only take up to 0.42 % volume of the nanocomposites. This small value is consistent with prior research on nanodielectrics with SCA functionalised nanoparticles. Therefore, the much thicker particle/polymer interaction region is commonly proposed to be the key factor in determining the bulk properties rather than a thin layer of SCA [1, 3, 5].

TABLE 2
DATA FROM TGA RESULTS

multiplication factor	Weight remain (%)	Difference (%)	C8-M thickness (nm)	C8-M volume ratio (%)
0	97.0	0	0	0
1	95.4	1.6	0.9	0.17
7	93.2	3.8	2.1	0.41
15	93.2	3.8	2.1	0.41
30	93.1	3.9	2.2	0.42

B. *AC breakdown results*

The AC breakdown result of each system is shown in Fig. 3. It is obvious that all samples present near-identical AC breakdown behaviours, apart from C8-30, which shows a slightly better performance. Both insufficient surface treatments and thick layers of SCA may lead to a reduction in AC breakdown strength [1, 11]. Compared to C8-1, although more hydroxyl groups are displaced by SCA in C8-7, C8-15 and C8-30, a potential thick layer of SCA surrounding the AlN surface might neutralise the benefits from the reduction of the density of hydroxyl groups. On the other hand, unlike the epoxide-terminated SCA used in, e.g. [3], where the organofunctional groups of SCA can form covalent bonds with the epoxy matrix, C8 groups do not have strong interactions with polypropylene. Hence the amount of C8-M used in surface treatments has little effect on the polymer morphology, and in turn, the AC breakdown strength of AlN/polypropylene nanocomposites.

C. *Dielectric response*

The dielectric response was tested at 90 °C with dry samples. All samples were dried in a vacuum oven at 80 °C for 3 days prior to the test to minimise the water absorption issue. The real permittivity of each sample seems to be a flat line with a slight increase within the tested frequency range when plotted against frequency, and a flatter increase can be observed in C8-1. So, the real permittivity at 1 kHz of each sample was plotted in Fig. 4a for convenience, where a bathtub-like trend can be observed. The higher real permittivity of C8-1 than that of C8-7 and C8-15 can be explained by the insufficient amount of SCA used during

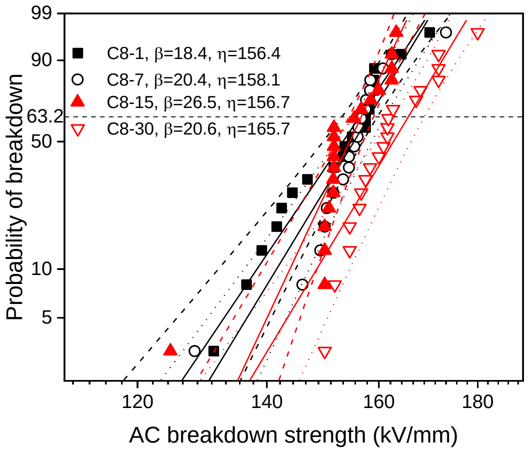

Fig. 3. AC breakdown strength of each system

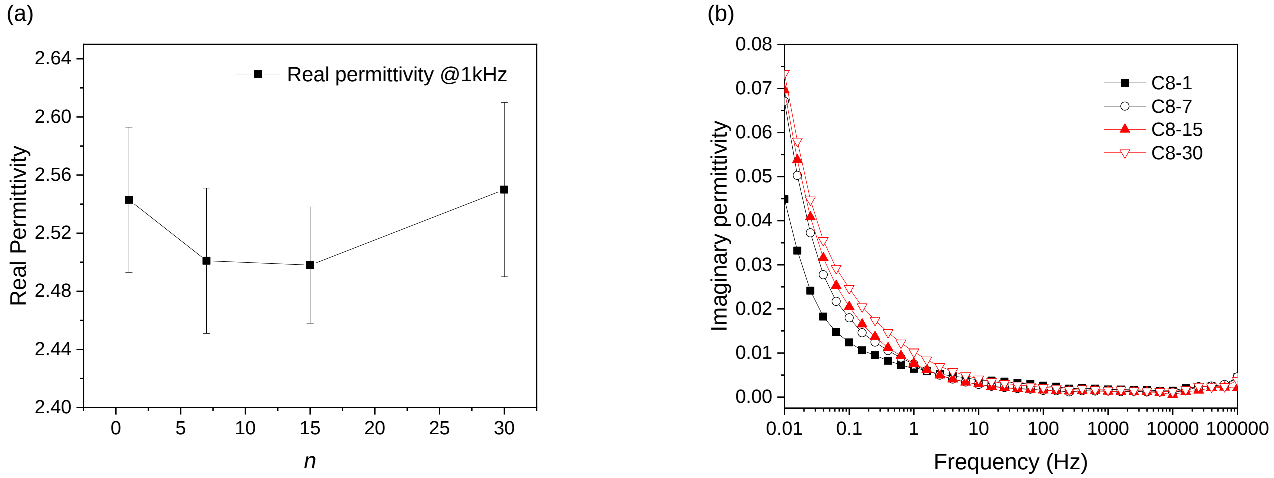

Fig. 4. (a) Real permittivity at 1 kHz and (b) imaginary permittivity of each system

the surface treatment. There is still a considerable ratio of -OH groups on the nanoparticle surface without grafted C8-M, and these -OH groups can lead to an increased real permittivity [1, 6]. C8-30 shows the highest real permittivity, which could be related to the excess of SCA used during the surface treatment, and more non-grafted by-products are remaining in the system. However, taking into account the error from the equipment and different samples (up to about ±4 %), the differences of the real permittivity between each system can be considered as insignificant. This behaviour is different from [1], where the real permittivity shows a progressive decrease when the loading amount of the epoxide silane is increasing in the nanosilica/epoxy system. These indicate that the density of the polar bonding sites resulting from the filler type, and the filler/polymer interaction that introduced by SCA can be the key factors in determining the dielectric response, rather than the minor change on the thickness of the SCA layer on the filler surface.

The imaginary permittivity of each system shows an upturn at low frequency and the C8-1 system present to have the lowest magnitude. That means the SCA layers might contribute more to the increased imaginary permittivity than the non-displaced -OH groups, even C8 groups are less polar than these non-displaced groups. These results could be related to the thick SCA layers with complex structures are formed surrounding the AlN or the conductivity contribution introduced by C8 endings on the nanoparticle surface. But overall, the amount of C8-M used during the surface treatment will not lead to significant differences in the imaginary permittivity from 0.01 Hz to 100 kHz.

IV. CONCLUSIONS

Nano AlN was surface functionalised with four different amounts of C8-M silane. Nanoparticles were tested by TGA, and a saturation point can be reached when increase *n* from 1 to 7 and no further increase of the grafted C8-M can be observed. AC breakdown and dielectric spectroscopy tests were performed on four different nanocomposites with 10 wt. % of AlN. The results show that the properties of the C8-M layer on the AlN surface have little effect on the dielectric properties of polypropylene nanocomposites, which means for composites used in present work (AlN/C8-M/polypropylene), there is a considerable error tolerance in terms of the amount of SCA used.

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